An X-ray Crystallographic Study of a Polymeric Diamido-Thallium(I) Complex Possessing Tl-Tl Interactions, $[K_2\{O{=}C(NAr)_2Tl\}_2]_\infty$, Ar – $C_6H_3Pr^i_2$-2,6.

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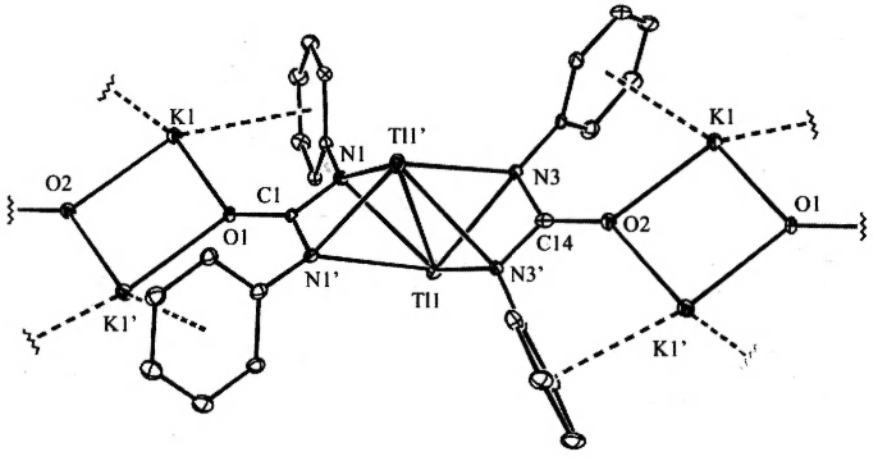
ABSTRACT

The crystal structure of the diamido-thallium(I) complex, $[K_2\{O{=}C(NAr)_2Tl\}_2]_\infty$, Ar = $C_6H_3Pr^i_2$-2,6, shows it to consist of dianionic, dimeric units (possessing Tl-Tl interactions) that are aggregated into linear polymeric chains through K-O and K-η^6-arene interactions.

Figure 1. Molecular structure of $[K_2\{O{=}C(NAr)_2Tl\}_2]_\infty$ **I** (isopropyl groups and hydrogens omitted for clarity, 20% ellipsoids). Key geometric parameters (Å, °): Tl(1)-N(1) 2.619(5), Tl(1)-N(3)' 2.670(5), Tl(1)-N(3) 2.741(5), Tl(1)-Tl(1)' 3.2992(6), K(1)-O(1) 2.625(4), O(1)-C(1) 1.309(9), N(1)-C(1) 1.354(6), O(2)-C(14) 1.261(11), N(3)-C(14) 1.375(7), N(1)-Tl(1)-N(3)' 109.58(16), N(1)-Tl(1)-N(3) 86.97(12), N(3)'-Tl(1)-N(3) 49.64(19), N(1)-Tl(1)-Tl(1)' 56.17(10), N(3)'-Tl(1)-Tl(1)' 53.42(11), N(3)-Tl(1)-Tl(1)' 51.47(11), N(1)'-C(1)-N(1) 114.9(7), N(3)'-C(14)-N(3) 111.5(8), K(1)-arene centroid 2.993(4), K(1)'-arene centroid 2.900(4). Symmetry operation: ' -x+1/2, -y+1/2, z.



COMMENT

The preparation of thallium(I) amides which exhibit metallophilic Tl-Tl interactions is a topical subject /1/. In the course of our work into the preparation of bulky amidinato-thallium(I) complexes /2/, we observed the low yield formation of the diamido-thallium(I) complex, $[K_2\{O=C(NAr)_2Tl\}_2]_\infty$, Ar = $C_6H_3Pr^i_2$-2,6, **I**, in the reaction of $K[Bu^tC(NAr)_2]$ with TlBr. Complex **I** likely arises from contamination of the potassium amidinato starting material with the doubly deprotonated urea complex, $K_2[O=C(NAr)_2]$. The molecular structure of **I** (Figure 1) shows it to consist of dianionic, dimeric units which possess Tl-Tl bonds that are in the known range [2.734 – 3.887 Å] /3/. The Tl_2 units are bridged by two chelating diamide ligands with unexceptional Tl-N distances. The dimeric units are associated into infinite 1-dimensional polymeric chains through coordination of each potassium counter-ion by two O-centres and two η^6-arene interactions.

EXPERIMENTAL

$[K_2\{O=C(NAr)_2Tl\}_2]_\infty$ **I**:

The title compound was formed, reproducibly, as a low yield by-product in the reaction of $K[Bu^tC(NAr)_2]$, contaminated with small amounts of $K_2[O=C(NAr)_2]$, with TlBr in THF. The insolubility of the polymeric compound in all common deuterated solvents thwarted attempts to obtain NMR spectroscopic data. M.p. 133 – 135°C (dec. to Tl metal); IR ν/cm^{-1} (Nujol): 1599 (s), 1564 (m), 1322 (m), 1268 (m), 1172 (m), 1097 (m), 1017 (m), 796 (m), 751 (m); (MS/EI) m/z : 1244 [M^+, 28%], 622 [M^+/2, 100%]; acc. MS (EI) calc. for $C_{50}H_{68}O_2N_4K_2Tl_2$: 1244.4099, found 1244.4103.

Crystallography:

Table 1

$[K_2\{O=C(NAr)_2Tl\}_2]_\infty$

Formula	$C_{50}H_{68}K_2N_4O_2Tl_2$	Formula weight	1244.02
Crystal system	orthorhombic	Crystal size, mm	0.25x0.20x0.15
Space Group	*Fdd*2	*a*, Å	24.563(5)
b, Å	36.363(7)	*c*, Å	11.253(2)
V, Å^3	10051(4)	*Z*	8
Diffractometer	Nonius Kappa CCD	Temperature, K	150(2)
μ(Mo-K$_\alpha$), mm^{-1}	6.611	D_{calcd}, g cm^{-3}	1.644
F(000)	4896	θ_{max},°	27.48
Reflns meas.	38571	Reflns unique	5703
$R(F^2)$, $R_W(F^2)$ ($I > 2\sigma(I)$)	0.0297, 0.0570	ρ, e Å^{-3}	1.684 (near Tl(1))
G.O.F.	1.052	No. obs/No. para	5703/282
Programs used	SHELX-97 [4]	Deposition number	CCDC 609041

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REFERENCES

1. L.H. Gade, *Dalton Trans.*, **2003**, 267.
2. C. Jones, P.C. Junk, J.A. Platts, D. Rathmann and A. Stasch, *Dalton Trans.*, **2005**, 2497.
3. As determined from a survey of the Cambridge Crystallographic Database, May, 2006.
4. G.M. Sheldrick, *SHELX-97*, University of Göttingen, Germany, 1997.